How to create nanomaterial
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November 30, 2003

Part I:
Title: Science of new nano-scale material
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The seventh line from the bottom on page 17 to line 8 on page 21 is translated.

3.4.3 Mechanical Dispersion of Inorganic Fine Particles

It has been known long that the characteristics of materials are improved by homogenously dispersing inorganic fine particles of silica gel or the like in organic materials such as plastics. As some of such typical examples, a resin obtained by immerse calcium carbonate or glass fibers in a plastic, rubber kneaded with carbon black, etc. are known. This method has been employed[23)] as an effective method for improving the rigidity or sizing accuracy of materials, or as an industrially important factor, namely, a means for reducing material costs. The use of organic/inorganic hybrid materials as described above has been particularly effective, when plastics have been handled as disposal or as auxiliaries since they are not stock materials such as iron and steel, although plastics have been still very industrially important materials. However, in association with the maturation of

the industries, mainly in the field of electronic devices, keen attentions have been paid to materials small in size and more homogenous materials having specific functions. To satisfy these demands, trials to disperse inorganic fillers with smaller diameters have been made[26]. In case where particles of nano order are used in place of particles of micron order, firstly, careful attentions are paid to 1) the agglomerating force of fine particles and 2) consumed energy for pulverizing the particles. The properties of a material are determined based on the binding of the surface of the material to the interior thereof and a balance in force between the surface of the material and an external. If the unevenness of the surface of the material is large, or if the particle size of the material is small, the binding force of the surface of the material to the interior thereof becomes relatively small so that the surface of the material becomes active.

As one of the methods for preparing organic/inorganic composites of nano order, inorganic porous bodies designable in strength are kneaded in an apparatus capable of shearing like an extruder, and are dispersed by increasing the shear to a value more than the previously designed strength of the porous bodies[25]. In one of typical methods, a pellet-like resin and porous inorganic particles are charged in an extruder or a kneader so as to

pulverize the particles[25]. Fig. 24 illustrates the steps of preparing such a nano composite. If inorganic particles are poor in affinity to an organic material as a dispersing medium, it is easily anticipated that the inorganic particles will be agglomerated to one another while being kneaded, as shown in Fig. 24.

Fig. 24 Conceptual Diagram for Preparing Nano Composite

a: Pseudo-phase-separated porous material (prepared from silica sol)

b: Resin used (pellet)

c: Kneading

d: Molding

e: Fine particles

f: Pellet

g: Agglomeration

h: Pseudo-phase-separated porous material

i: Pellet

j: Purverization

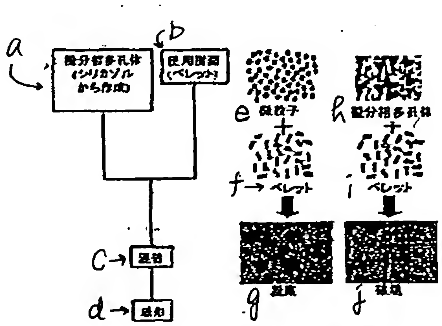

図24 ナノコンポジット調整概念

When a constant shear force is applied to a material, whether or not the material is bucked depends on whether or not the shear strength of the material is larger or smaller than an external shear force. For example, a shear force which a material receives in an ordinary extruder is about 10.8 X 10^2 MPa, which is a substantially similar value to shear forces to Japanese cryptomereia (24.5 MPa), polypropylene (39.2 MPa) and a glass plate (88.2 X 10^3 MPa), while cast iron shows a compression strength of 64.9 X 10^6 MPa. Therefore, there have been some reports on trials to grind Japanese cryptomereia in an extruder, but no report on a trial to grind cast iron in an extruder.

The inorganic porous bodies described in the previous section can have a shear strength of about 10.8 MPa, if controlled within a range where the spinodal phase separation is not allowed to proceed, and thus can be pulverized in an apparatus like an extruder.

Fig. 25 Dispersed State of Pseudo-Phase-Separated Porous Material in Resin (Added amount of pseudo-phase-separated porous body 5wt%)

a: PBT/SiO_2 pseudo phase porous material

b: PC/SiO_2 pseudo phase porous material

c: PS/SiO_2 pseudo phase porous material

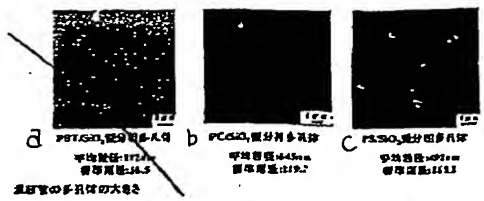

図25 樹脂中の擬分相多孔体分散状態 (擬分相多孔体添加量5wt%)

The circles shown on the left and lower side in Fig. 25 indicate the particle diameters of the inorganic porous bodies before subjected to pulverization. Since the diameter of the particles is 100 μm, the particles are supposed to be very large, if drawn according to this scale. The result of such particles dispersed in an extruder is shown on the right side from the center of the drawing. When this is sufficiently examined, it is possible to disperse finely pulverized inorganic particles in a plastic, and also possible to improve the rigidity or other characteristics of the resultant material without decreasing the strength thereof.

The problem of this method is that the fine particles of the inorganic porous body are not pulverized but are kneaded, in the following cases: 1) the breaking strength distribution of the inorganic porous body is large, and 2) the shear stress distribution of the kneader is large. For example, in the breaking-compression strength test of pseudo-phase-separated porous bodies, a slight variation in

strength is observed in the material, as shown in Fig. 26.

Fig. 26 Result of Compression Strength Distribution of Pseudo-Phase-Separated Porous Body

a: Average value

b: Standard deviation

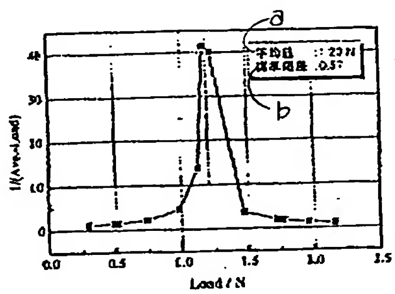

図 26 擬分相多孔体の圧縮強度分布結果（島津製小圧縮試験機 MCTN-500）

Further, the shear stress distributions of the kneading disc and the rotor segment of a twin-screwed extruder, and the shear stress distribution of the rotors of a continuous kneader are shown in Fig. 27. It is found that some distributions are observed in the stress-applying sides[27).

Fig. 27 Distribution of Shear Stress

a: Kneading disc

b: Rotor segment

c: Rotor

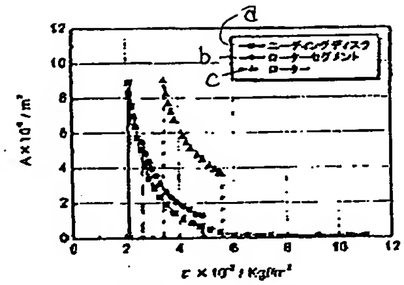

図27 剪断応力の分布

When a resin and pseudo-phase-separated porous particles are kneaded in an extruder, there is a variation in shear stresses which are applied to the particles by the particles which have passed through a portion having a smaller sectional area and the particles which have passed through a portion having a larger sectional area.

Fig. 26, showing the results of the compression strength tests, indicates a pressure applied to the pseudo-phase-separated porous body on the axis of abscissa, and an inverse number of a difference between the average value of the load and the crushed particles on the axis of ordinate. From the results of the compression tests shown in Fig. 26, it is found that there is a width in the crushing load on the pseudo-phase-separated porous particles, that the particles are not crushed by an even strength, and that the crushing strength differs depending on each of the particles. Particularly when the temperature of the extruder is relatively high, and when the strength of the

shear is insufficient, the pseudo-phase-separated porous particles are not pulverized but are kneaded (see the left side of Fig. 28). When the kneading temperature is adjusted to apply a relatively strong shear, an improved dispersed state of the particles as shown on the right side of Fig. 28 is observed.

Fig. 28 Dispersed State of Pseudo-Phase-Separated Porous Particless in PS, Found at Adjusted Kneading Temperature

Accordingly, it is considered that, if homogeneous kneading becomes possible, the pseudo-phase-separated particles can be more uniformly dispersed. The conditions and results of kneading of polystyrene (PS) and an ethylene-vinyl alcohol copolymer (EVOH) in a laboplast mill (Toyo Seiki) are described below.

EVOE as a resin was kneaded for 2.5 minutes at 180°C which was the set temperature of an apparatus, i.e., 5°C higher than the melting temperature of EVOH (175°C). While EVOH and SiO_2 were being kneaded at 180°C, the resin was heated due to shearing in association with the kneading, so that the temperature of the resin was increased to a

temperature of 200 to 204°C. During the kneading time (2.5 minutes) within this temperature range, the torque was decreased by about 2 Nm immediately after the start of kneading, and the torque was increased about 30 seconds after and then was kept constant. The value of the torque was from 32 to 34 Nm. The state of the dispersion of EVOH/SiO_2 prepared under these conditions was observed with SEM. The photograph taken with SEM is shown in Fig. 29, and the particle diameter distribution obtained by the measurement of the diameters of the particles from the SEM photograph is shown in Fig. 30.

Fig. 29 Dispersed State of EVOH/SiO_2
(SEM photograph of a magnification of 5,000)

Fig. 30 Particle Diameter Distribution of
Dispersed EVOH/SiO_2

a: Ratio

b: Diameter of dispersed particle

c: Sample: EvOH/SiO_2
Content: SiO_2 5wt%
Average particle diameter 74.7nm
Standard deviation

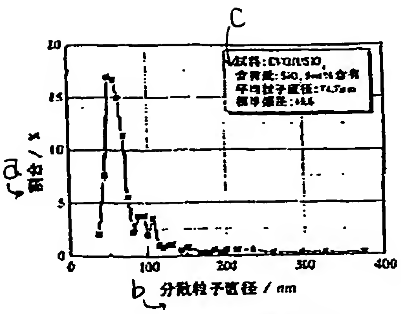

図30 EVOH/SiO_2の分散粒子径分布

From the results of Figs. 29 and 30, it was found that the sample of EVOH/SiO_2 had an average particle diameter of 74.7 nm, and that the ratio of the particles with a particle diameter of 50 to 60 nm had the largest distribution, relative to the number of all the particles counted on the SEM photograph. Similarly, the state of the dispersion of a sample comprising PS as a resin and 50 wt.% of pseudo-phase-separated porous particles was observed. The sample was obtained by kneading at a kneading temperature of 180°C and at a screw rotation number of 300 rpm for 2.5 minutes. The distributions of Si elements and C elements were observed with SEM.EDX, and were shown in Fig. 31.

Fig. 31 Distribution of Si Elements in PS/SiO_2 (containing 50 wt.% SiO_2)

While the boundaries between the silica particles and

the resin were not clearly observed, both the resin and the silica were not present as masses, but they coexisted in the sample.